Waste Management and Treatment Technology – Part 2

WATER SOFTENING

- removal of hardness
  - » Hardness is?...

    primarily Ca, Mg, plus Fe, Mn, St, Al
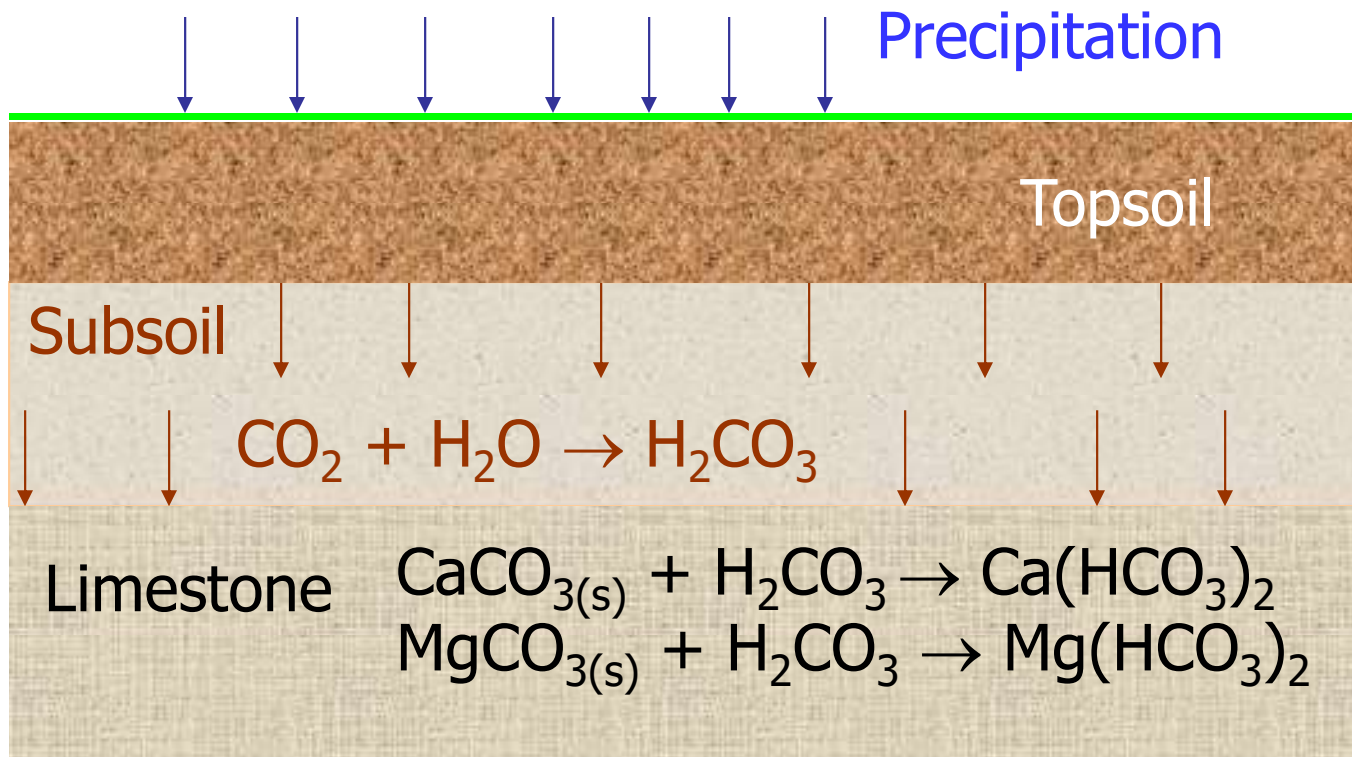
- How is Softening done?...

    Precipitation of Ca and Mg, or
    Ion exchange of Ca / Mg with ion such as Na

Why bother?

- Hardness in 300-500 mg/l as $CaCO_3$ range considered excessive
    high soap consumption
    scaling in heating vessels and pipes
- Even > 150 mg/l may result in consumer objection
- 60-120 mg/l as $CaCO_3$ is considered a moderate amount

Formation of Hardness

Precipitation

Topsoil

Subsoil

$$CO_2 + H_2O \rightarrow H_2CO_3$$

Limestone

$$CaCO_{3(s)} + H_2CO_3 \rightarrow Ca(HCO_3)_2$$
$$MgCO_{3(s)} + H_2CO_3 \rightarrow Mg(HCO_3)_2$$

Hardness

- Carbonate Hardness
  - » Often called "temporary hardness" because heating the water will remove it. When the water is heated, the insoluble carbonates will precipitate and tend to form bottom deposits in water heaters.
  - » Ca^{2+}, Mg^{2+} associated with HCO_3^-, CO_3^{2-}
  - » CH = TH or Total alkalinity, whichever is less

Hardness

- ● Non-Carbonate Hardness
  - » Called permanent hardness because it is not removed when the water is heated. It is much more expensive to remove non-carbonate hardness than carbonate hardness.
  - » Ca^{2+}, Mg^{2+} associated with other ions, Cl^-, NO_3^-, SO_4^{2-}
  - » NCH = TH - CH
  - » If Alkalinity $\geq$ Total hardness, then NCH = 0

Hardness Units

- milligrams per liter (mg/L) as calcium carbonate (most common)
- parts per million (ppm) as calcium carbonate

Exercise

- A water has a alkalinity of 200 mg/L as $CaCO_3$. The Ca^{2+} concentration is 160mg/L as the ion, and the Mg^{2+} concentration is 40mg/L as the ion. The pH is 8.1. Find the total, carbonate and noncarbonate hardness.

Solution

Determination of water hardness

- It is based on the fact that ethylenediamine tetra-acetic acid (EDTA) forms a chelated soluble complex with certain metal ions.
- Calcium and magnesium will complex with calmagite(indicator) forming a wine-red color.

- The pH must be maintained at 10.0 + 0.1. Therefore, when titrating, the color will change from wine-red to blue at the end point.
- Interference of other metal ions is prevented by adding inhibitors such as sodium cyanide or sodium sulfide, both being quite toxic.
- Normally for potable water no inhibitor is needed.

Procedure

- Standardize against the standard calcium carbonate, and calculate mg $CaCO_3$/ml EDTA
    1. Prepare 0.01M EDTA solution (weigh 1.8615g EDTA and mark up to 500ml in V. flask)
    2. Add 25ml Standard $CaCO_3$ solution (1mg/ml) + 25ml DI water into a 250 ml E-flask.
    3. Add 2 ml buffer solution. (contain ammonia)

4. Add 2 drops Eriochrome Black T indicator(calmagite)
5. Titrate with EDTA until a bright blue color appears.
6. Repeat the same procedure in triplicate.
7. Repeat procedure 2 – 6 with the following sample

Calculation

- mg/l hardness = $\dfrac{\text{ml EDTA x B x 1000}}{\text{ml sample}}$

where B = mg $CaCO_3$/ml EDTA was determined standardization.

LIME - SODA ASH SOFTENING

- Addition of lime, $Ca(OH)_2$, & soda ash, Na_2CO_3 causes precipitation of Ca, Mg

- Lime often added as CaO, quick lime
  - » $CaO + H_2O \rightarrow Ca(OH)_2$

Softening Reactions

- 1. Neutralization of carbonic acid

- 2. Precipitation of carbonate hardness due to calcium

- 3. Precipitation of carbonate hardness due to magnesium

- 4. Precipitation of noncarbonate hardness due to calcium

- 5. Precipitation of noncarbonate hardness due to magnesium

Solubilities

- $Ca(OH)_2$ is very soluble, **$Mg(OH)_2$ is not**
- $MgCO_3$ is very soluble, **$CaCO_3$ is not**
  - » $CaCO_3$ and $Mg(OH)_2$ are <u>relatively</u> insoluble
- Practical limits
  - ✓ $CaCO_3$: ~ 30 mg/l as $CaCO_3$
    - 0.6 meq/l
  - ✓ $Mg(OH)_2$: ~ 10 mg/l as $CaCO_3$
    - 0.2 meq/l

Removal by precipitation

- Is complete removal possible?...

No, lime-soda ash softening
cannot remove all hardness

What about CO_2?

- $CO_2 + Ca(OH)_2 \rightarrow$ **$CaCO_3$** $+ H_2O$

CO_2 must be considered because it
consumes lime

Effectiveness

- 80-100 mg/l as $CaCO_3$ is usually considered acceptable result of lime-soda ash softening,

  » as long as Mg is < 40 mg/l as $CaCO_3$

 ✓any more causes scaling in heating vessels

Stoichiometry Table

● meq of lime and soda ash to remove a
  meq of X <u>initially present</u>

X	Lime	Soda Ash
CO_2	1	0
$Ca(HCO_3)_2$	1	0
$Mg(HCO_3)_2$	2	0
$MgCO_3$	1	0
$MgSO_4$	1	1
$CaSO_4$	0	1

Membrane Processes

•A membrane is a selective barrier that permits the separation of certain species in a fluid by combination of sieving and diffusion mechanisms

•Membranes can separate particles and molecules and over a wide particle size range and molecular weights
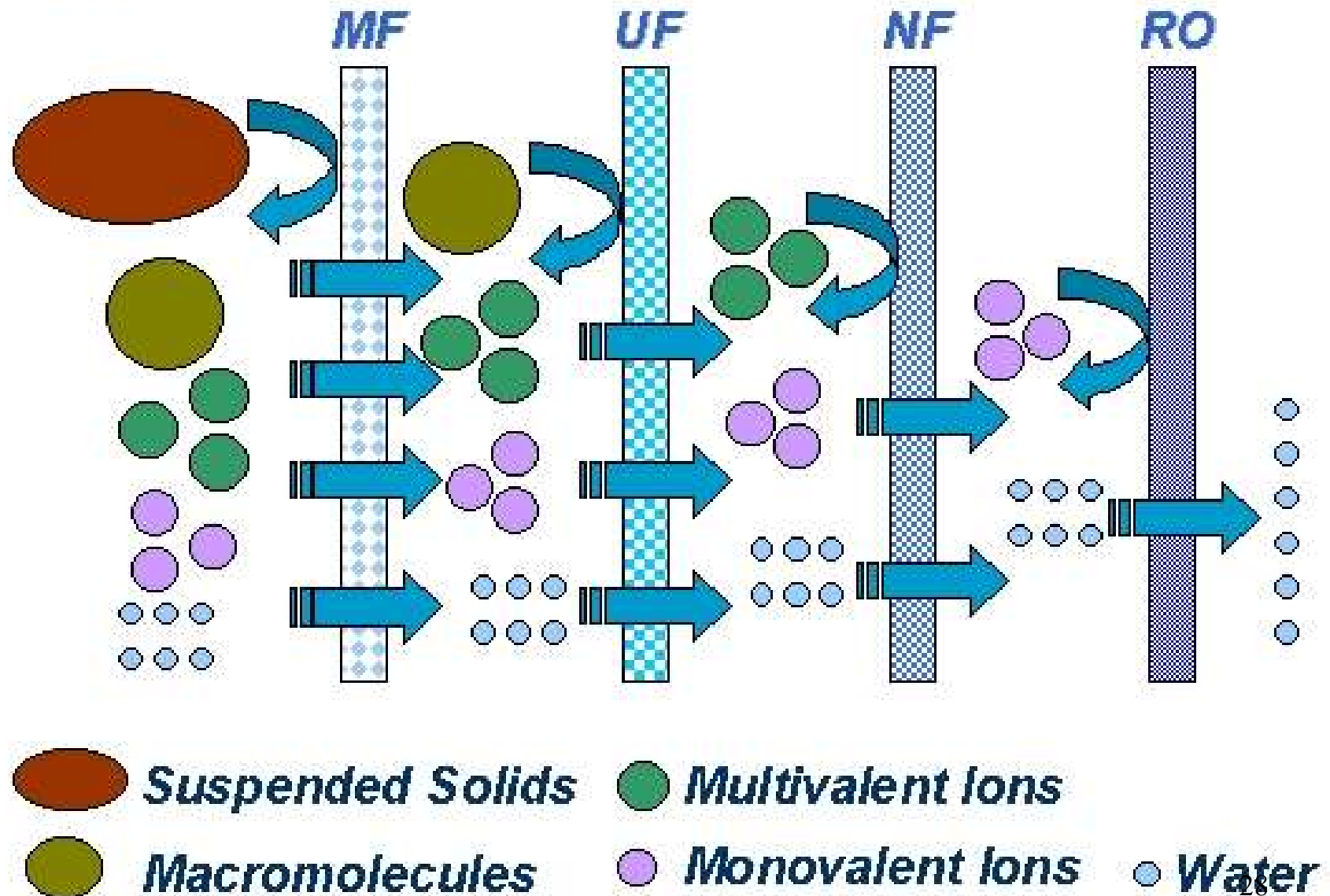
25

Membrane Separation

Membrane

Feed

Permeate

○ : Solute Particle   ● : Solvent

26
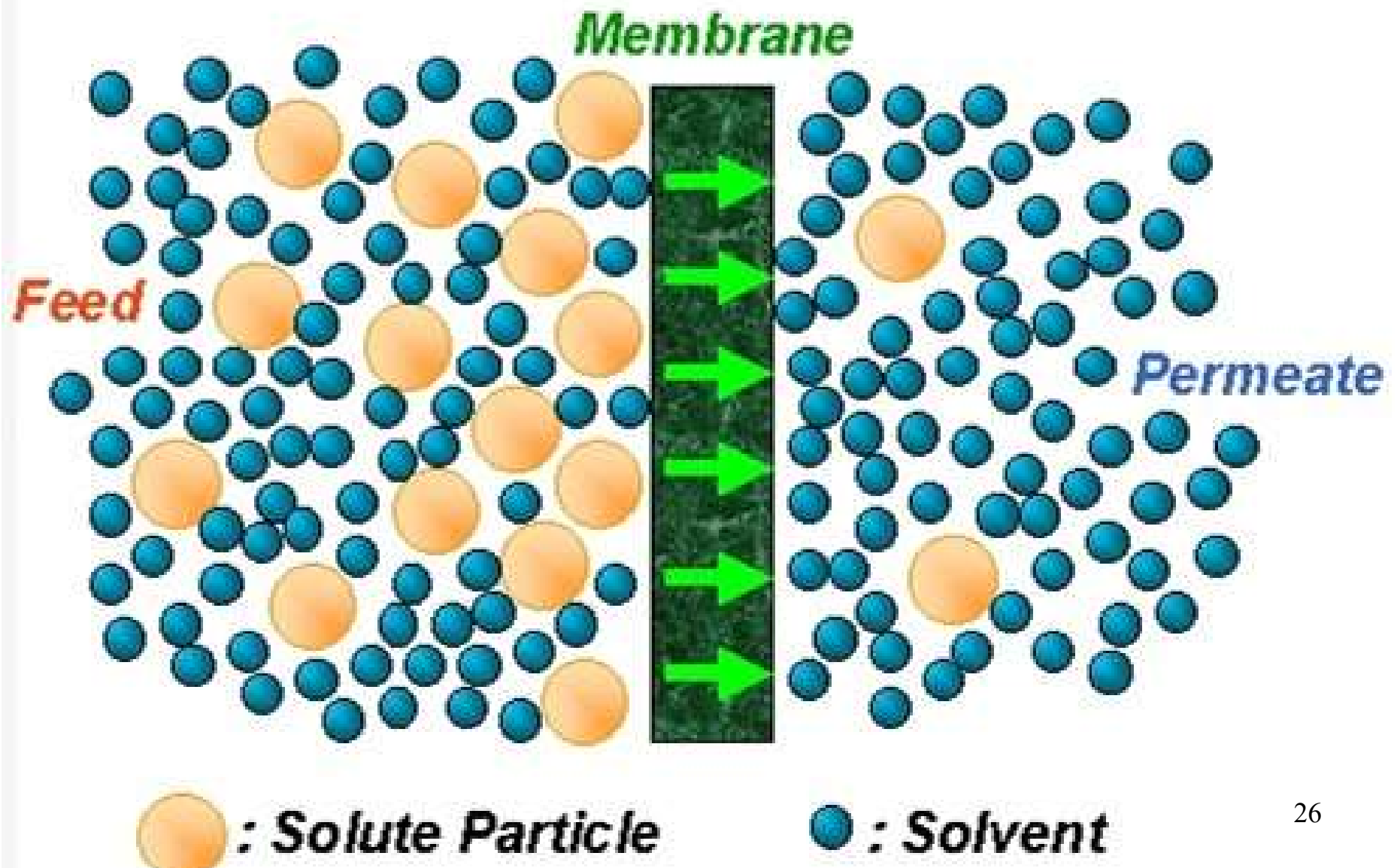
Membrane Processes

Four common types of membranes:

Reverse Osmosis

Nanofiltration

Ultrafiltration

Microfiltration

27

Types of Membrane

MF   UF   NF   RO

Suspended Solids   Multivalent Ions

Macromolecules   Monovalent Ions   Water

SIZE, MICRONS		0.001	0.01	0.1	1.0	10	100	1,000

RELATIVE SIZE OF VARIOUS MATERIALS IN WATER

VIRUSES
BACTERIA
AQUEOUS SALTS
ALGAE
HUMIC ACIDS
CYSTS
SAND
METAL IONS
CLAYS
SILT
ASBESTOS FIBERS

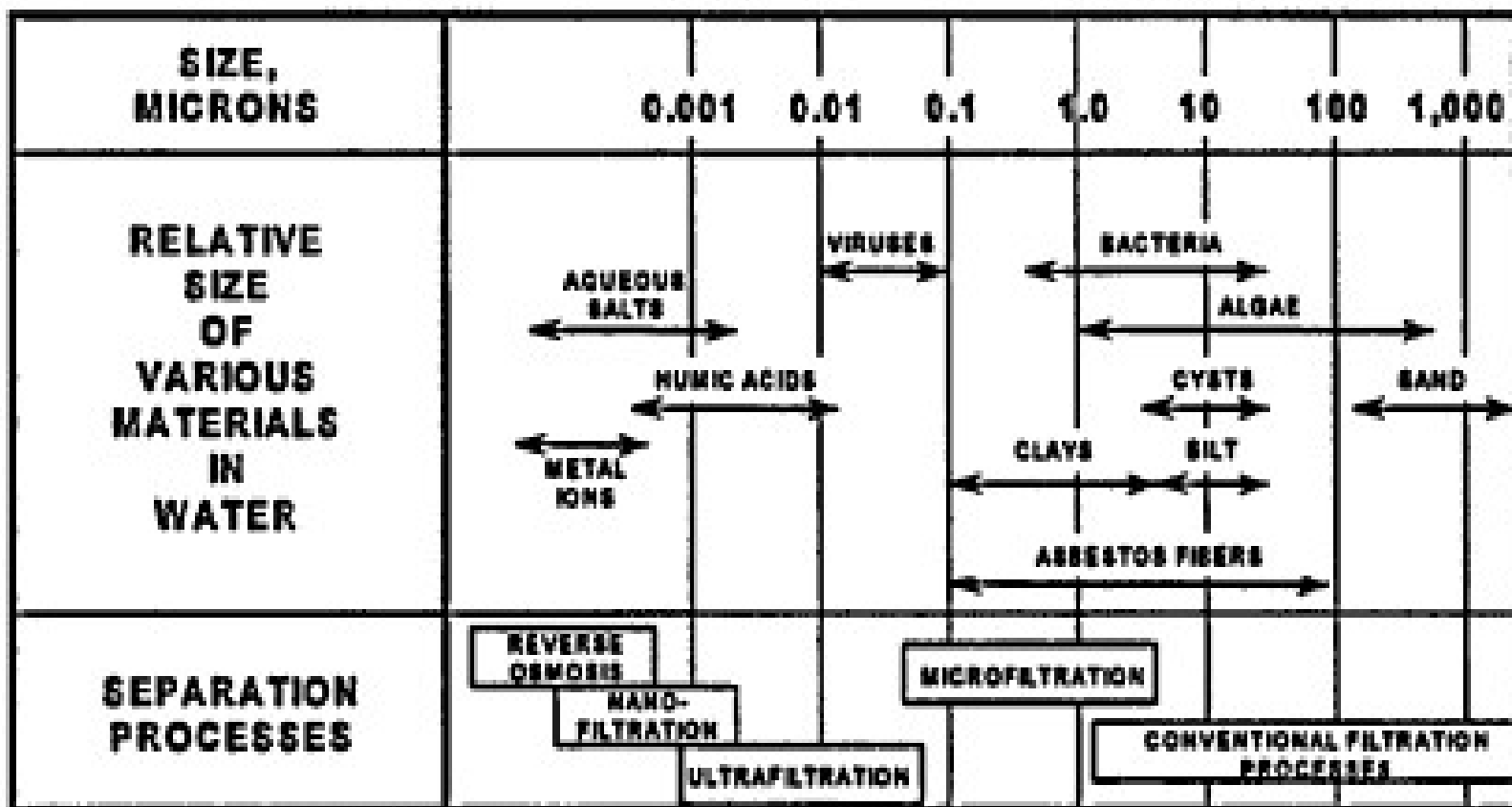SEPARATION PROCESSES

REVERSE OSMOSIS
NANO-FILTRATION
MICROFILTRATION
ULTRAFILTRATION
CONVENTIONAL FILTRATION PROCESSES

29

Nanofiltration is a complementary process to reverse osmosis, where divalent cations and anions are preferentially rejected over the monovalent cations and anions. Some organics with MW > 100 -500 are removed   There is an osmotic pressure developed but it is less than that of the R.O. process.

Microfiltration and Ultrafiltration are essentially membrane processes that rely on pure straining through porosity in the membranes. Pressure required is lower than R.O. and due entirely to frictional headloss

30

Reverse Osmosis

In normal osmosis:

●Water molecules move from a region of higher concentration to a region of lower concentration through a partially permeable membrane

In reverse osmosis:

●Water molecules are forced to move from a region of lower concentration to a region of higher concentration by applying a huge amount of pressure

31

Reverse Osmosis

Result:
● The solute is retained on the pressurised side of the membrane
● The pure solvent is allowed to pass to the other side
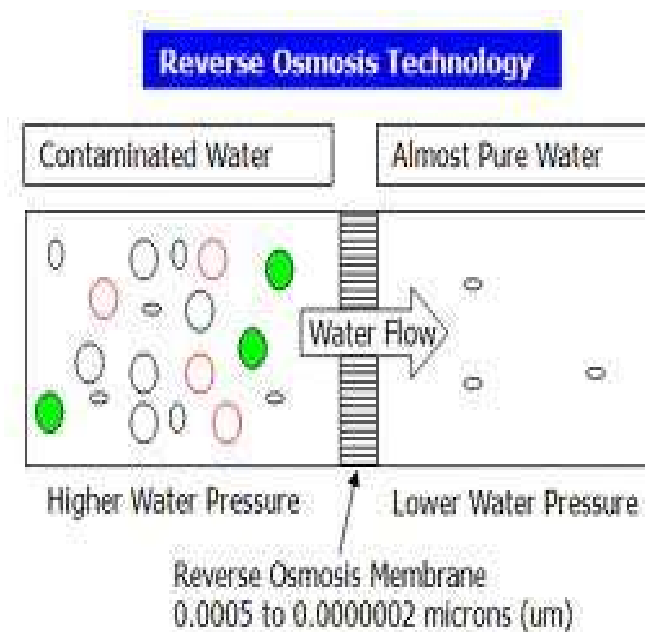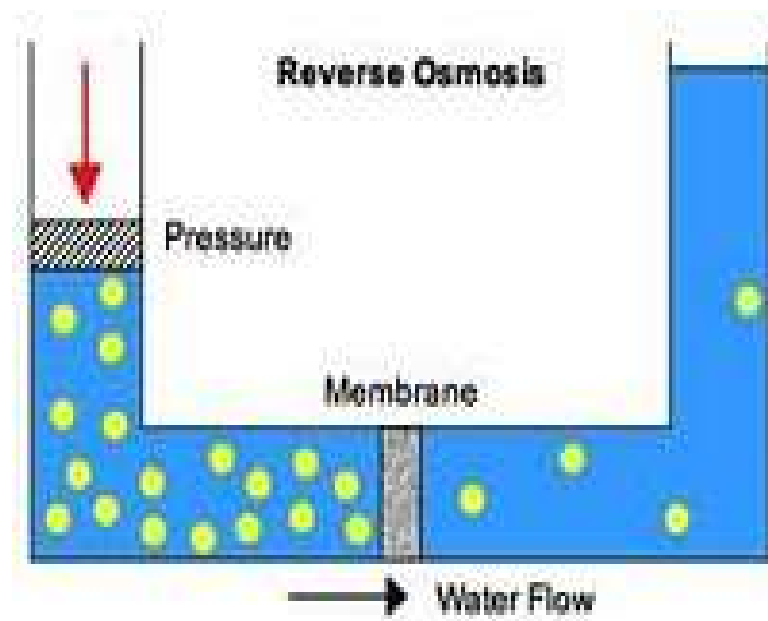
Membrane used:
● Designed to only allow water molecules to pass through
● Does not allow larger molecules such as salt ions to pass through

32

Reverse Osmosis

- The pressure applied must overcome the natural osmotic pressure.
- Eg. 600-1200 psi of pressure must be used for seawater, as it has a natural osmotic pressure of 390 psi.

*Osmotic pressure: The tendency for the solvent to flow through the membrane until there is the same concentration of the solvent on both sides of the membrane

33

Process of Reverse Osmosis

Reverse Osmosis

Pressure

Membrane

Water Flow

Reverse Osmosis Technology

Contaminated Water | Almost Pure Water

Water Flow

Higher Water Pressure | Lower Water Pressure

Reverse Osmosis Membrane
0.0005 to 0.0000002 microns (um)

34

NEWater

NEWater Plant

35

Removal of Specific Constituents

- Arsenic
  - » A semi-metal element. It is odorless and tasteless. It enters drinking water supplies from natural deposits in the earth or from agricultural and industrial practices.
  - » It is also used in paints, dyes, metals, drugs, soaps, and semi-conductors. Agricultural applications, mining, and smelting also contribute to arsenic releases in the environment.

36

Health Effects

- May experience skin damage or problems with their circulatory system, and may have an increased risk of getting cancer.

- Maximum contaminant level (MCL), at 0.010 mg/L or 10 ppb.

37

Treatment Strategies

- **Coagulation-Filtration**
  - » The efficiency and economics of the system are contingent upon several factors including the type and dosage of coagulant, mixing intensity, and pH.

  - » This process can be optimized to remove dissolved inorganic As(V) from water. The mechanism involves adsorption of As(V) to an aluminum or ferric hydroxide precipitate and removal by filtration.

38

- As(III) is not effectively removed because of its overall neutral charge under natural pH. Because As(III) is more difficult to remove than As(V), pre-oxidation is typically necessary.

- In general, optimized coagulation/filtration systems are capable of achieving over 90% removal of As(V).

39

Preoxidation Process

- 1. Chlorine(hypochlorite)

- 2. Permanganate

- 3. Ozone

40

- Example: Estimate the stoichiometric amount of hypochlorite in mg/L required to oxidize arsenic in groundwater with the following constituents:
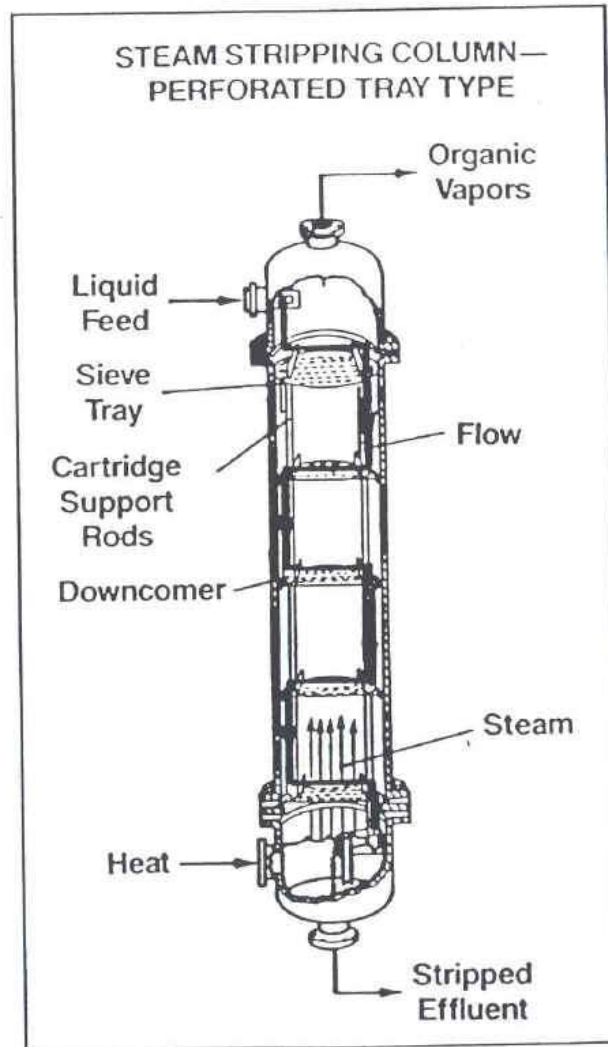- As(III) = 50µg/L, Fe(II) = 1.2mg/L

Synthetic Organic Chemical(SOC)/ Volatile Organic Chemical(VOCs)

- SOC. E.g. Pesticides, polycyclic aromatic hydrocarbons, polychlorinated biphenyls

- VOC – Compounds with high vapor pressure to evaporate readily.
- E.g. Petroleum products, halogenated compounds.

42

Treatment Strategies

- **Steam stripping**
  - » uses steam to evaporate volatile organics from aqueous wastes. It essentially is a continuous fractional distillation process carried out in a packed tower.
  - » Clean steam provides direct heat to the column in which gas flows from the bottom to the top of the tower.

43

STEAM STRIPPING COLUMN—
PERFORATED TRAY TYPE

Organic Vapors

Liquid Feed

Sieve Tray

Flow

Cartridge Support Rods

Downcomer

Steam

Heat

Stripped Effluent

STEAM STRIPPING

44

- The residuals are contaminated steam condensate, recovered solvent and stripped effluent. The organic vapors are sent through a condenser in preparation for further purification treatment.

- Steam stripping is used to treat aqueous wastes contaminated with chlorinated hydrocarbons, aromatics (xylenes), ketones (acetone), alcohols (methanol) and high boiling point chlorinated aromatics (pentchlorophenol).

45

Granular Activated Carbon

- Mass-transfer process in which the chemical is bonded to the solid. (adsorption)
- The chemical penetrates into the pore of the solid physically or chemically.
- The number of active sites is finite and becomes saturated over time. Regenerated by heating with hot air or steam.

46

Adsorption Isotherm

- Used to determine mass of solute adsorbed per mass of activated carbon, (mg/g)
- Conducted at constant temperature and pH.

47

Adsorption Isotherms

Add Same Initial Target Chemical Concentration, C_{init}, in each
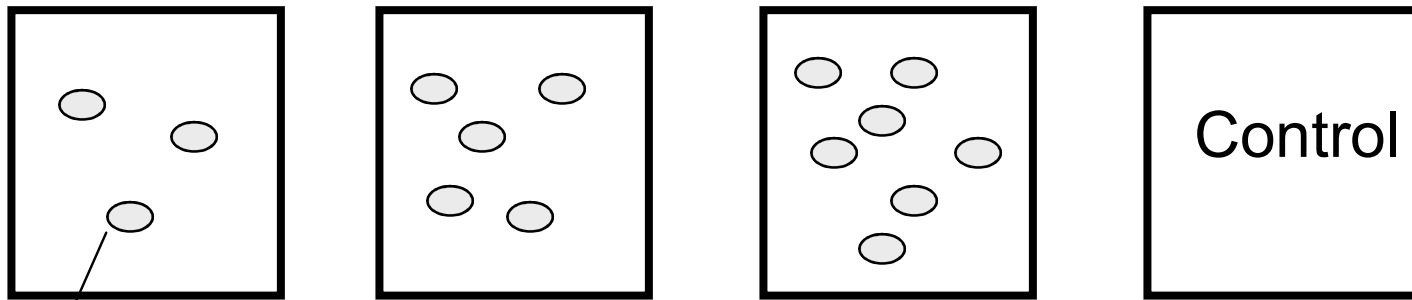
Different activated carbon dosage, C_{solid}, in each

$$q_{fin}\left(\frac{\text{mg}}{\text{g}}\right) = \frac{c_{init} - c_{fin} \quad (\text{mg/L})}{c_{solid} \quad (\text{g/L})}$$

An adsorption 'isotherm' is a *q* vs. *c* relationship at equilibrium